[CONTRIBUTION FROM THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

Cyclopropanes from Allylic Chlorides *via* Hydroborination

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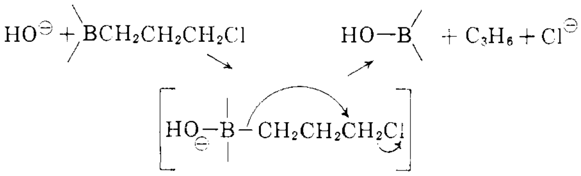
The reaction of a β-alkyl or β-arylallyl chlorides with diborane followed by basic hydrolysis of the crude reaction product mixture affords the corresponding substituted cyclopropane.

In a previous paper[1] it was shown that the addition of diborane to allyl chloride in ethereal solvents resulted in the formation of a mixture γ-chloropropylborane derivatives. Basic hydrolysis of each of these derivatives produced cyclopropane

$$CH_2{=}CH{-}CH_2Cl \xrightarrow[B_2H_6]{R_2O} Cl_xB(CH_2CH_2CH_2Cl)_{3-x}$$

where $x = 0$, 1 and 2

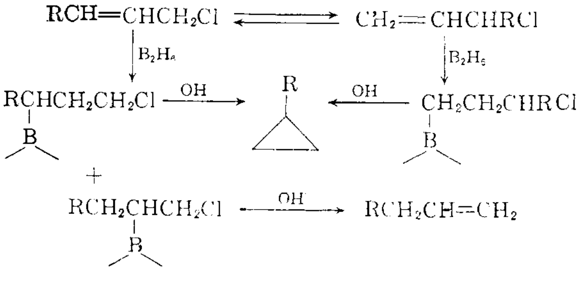
in high yield.

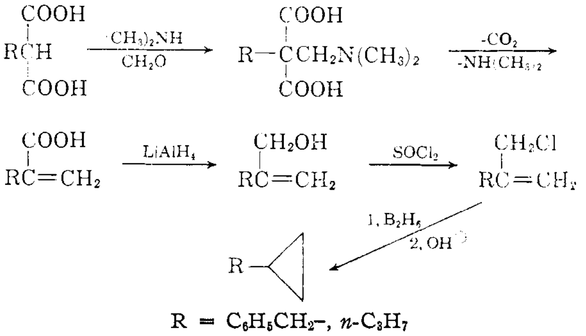


Similarly, vinyl chloride and diborane produced unstable β-chloroethylborane derivatives which thermally or hydrolytically decomposed to produce ethylene.

It appeared that this series of reactions could be extended to a relatively useful laboratory method for the preparation of cyclopropane and certain substituted cyclopropanes. That topic is discussed in the present paper.

Alkyl- and arylcyclopropanes were prepared from the corresponding β-alkyl or β-arylallyl chlorides. The use of the α- or the γ-substituted isomers (or an equilibrium mixture of the two) would have led to the formation of a mixture of substituted cyclopropane and isomeric olefin. This situation imposed a limitation upon the usefulness of the method described here since β-substituted allyl halides are relatively difficult to obtain. Indeed, the β-methylallyl and the β-phenylallyl[2] halides are the only well characterized members of that series described in the literature. A reliable, if rather lengthy, method was developed for these starting materials and is outlined





$R = C_6H_5CH_2-$, $n\text{-}C_3H_7$

The substituted malonic acids were readily converted to the corresponding alkyl-(dimethylaminomethyl)-malonic acids. Decarboxylation to yield the corresponding α-alkylacrylic acids was then accomplished by the method of Mannich and Ganz.[3] Reduction of the substituted acrylic acids was carried out with excess lithium aluminum hydride in diethyl ether at the reflux temperature[4] and the resulting β-substituted allyl alcohols were carefully purified by distillation. Conversion of the alcohols to the corresponding chlorides was accomplished in high yield by the method of Frazer, *et al.*,[5] which involved the thermal decomposition of the sulfite esters in the presence of thionyl chloride. The Experimental section contains data pertinent to the characterization of the materials described above.

β-Phenylallyl acetate was prepared by the selenium dioxide oxidation of α-methylstyrene as described by Hatch and Patton.[2] The purified acetate was converted to the alcohol by basic hydrolysis and then to the chloride by the method of Frazer, *et al.*[5] Although this method was more time consuming than the direct allylic bromination of α-methylstyrene described by Hatch and Patton,[2] the latter method did not give high yields and the β-phenylallyl bromide was difficult to purify. The bromide was, however, converted to phenylcyclopropane in 50% yield.

Cyclopropanes were prepared from the corresponding β-substituted allyl chloride by treatment of the olefin with an excess (100%) of diborane at zero degrees in either diethyl ether or diglyme, followed by immediate hydrolysis with excess aqueous sodium hydroxide solution. The former solvent was employed with the higher boiling cyclopropanes (phenyl, benzyl, *n*-propyl). Cyclopropane and methylcyclopropane were prepared in diglyme solution from which they were

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[1] M. F. Hawthorne and J. A. Dupont, THIS JOURNAL, **80**, 5830 (1958).

[2] L. F. Hatch and T. L. Patton, *ibid.*, **76**, 2705 (1954).

[3] C. Mannich and E. Ganz, *Ber.*, **55**, 3486 (1922).

[4] For a compilation of examples of similar reductions see N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p. 350.

[5] M. J. Frazer, W. Gerrard, G. Machell and B. D. Shepherd, *Chem. and Ind.*, 931 (1954).

distilled directly. In no case was the intermediate γ-chloropropyl borane derivative isolated.

The hydrolysis reactions were quite exothermic and were accompanied by the evolution of hydrogen. The hydrogen was produced from hydrolysis of the B–H bonds present in the reaction mixture which in turn resulted from the use of excess diborane. The crude reaction products were probably a mixture of R_3B, R_2BH and RBH_2 species.

Hydroborination reactions were conducted on an 0.50-mole scale with allyl and β-methylallylchlorides. All other reactions were carried out on a 0.10-mole scale. Table I sets forth the yield data and characterization constants of the cyclopropanes prepared. Cyclopropane, methylcyclopropane and phenylcyclopropane prepared by the hydroborination reaction were identical to authentic samples in the infrared.

TABLE I

CYCLOPROPANES PREPARED FROM THE CORRESPONDING β-SUBSTITUTED ALLYL CHLORIDES

		B.p.		
Substituent	Yield, %	°C.	Mm. °C.	n^{25}D
H-	43	[a]		
CH_3–	71	[a]		
$CH_3CH_2CH_2$-	61	69–70	755[b]	1.3910
C_6H_5–	55	86	45[c]	1.5302
$C_6H_5CH_2$–	45	98–100	40[d]	1.5147

[a] Identified by vapor phase infrared spectrum; analysis by mass spectrometer indicated 99–100% purity. [b] H. Pines and W. D. Huntsman, THIS JOURNAL, **75**, 2311 (1953), report b.p. 69–70° (760 mm.) and n^{20}D 1.3926. [c] H. E. Simmons and R. D. Smith, *ibid.*, **81** 4256 (1959), report b.p. 69° (22) and n^{25}D 1.5309. [d] Ref. *c* reports b.p. 122–124° (107) mm. and n^{20}D 1.5132.

Seen as in Table I the yields of cyclopropanes which were obtained by this method were respectable but not high. It is possible that further work would render the method more economical for laboratory use.

An obvious extension of this cyclopropane synthesis was the attempted closure of a cyclobutane ring *via* hydroborination of 4-chlorobutene-1. Although hydroborination proceeded smoothly in this case the product would not eliminate chloride ion in the proper fashion even when maintained at 100° for a twelve-hour period.

Experimental

Materials.—All starting materials were commercial reagent grade chemicals or were prepared by conventional methods described in the literature. Diborane was prepared as described by Brown and SubbaRao.[6]

***n*-Propyl-(dimethylaminomethyl)-malonic Acid.**—Seventy-two grams (0.50 mole) of pure *n*-propylmalonic acid was neutralized (brom thymol blue indicator) by the slow addition of an aqueous 25% solution of dimethylamine. An additional 72 g. of *n*-propylmalonic acid was added and the resulting solution cooled to 0° with stirring. Aqueous formaldehyde (100 ml. of 33% solution) was added with cooling and stirring. The solution deposited 82 g. (41%) of crystalline *n*-propyl-(dimethylaminomethyl)-malonic acid, m.p. 109–110°, after standing overnight at room temperature.

Anal. Calcd. for $C_9H_{17}O_4N$: C, 53.18; H, 8.43. Found: C, 53.25; H, 8.20.

***α-n*-Propylacrylic Acid.**—To 80 g. (0.40 mole) of *n*-propyl-(dimethylaminomethyl)-malonic acid was added 100 ml. of water and sufficient 10% aqueous sodium hydroxide solution to render the solution neutral to brom thymol blue indicator. The resulting solution was refluxed overnight with a nitrogen atmosphere, cooled and acidified with 200 ml. of concentrated hydrochloric acid. The mixture was extracted four times with 100-ml. portions of ether, the combined extracts washed once with water, dried over magnesium sulfate and the solvent evaporated. *n*-Propylacrylic acid (30.5 g., 67%) was obtained by distillation with an efficient column, b.p. 75° (2.5 mm.) and n^{25}D 1.4330.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 63.30; H, 8.98.

***β-n*-Propylallyl Alcohol.**—To a solution of 15 g. of lithium aluminum hydride in 500 ml. of ether was added 30 g. (0.27 mole) of *α-n*-propylacrylic acid dissolved in 200 ml. of ether. The reaction was maintained at the reflux temperature during the addition and for 4 hours afterward. The mixture was then cooled and treated with methanol in the usual fashion. Acidification with dilute hydrochloric acid followed by extraction with three 200-ml. portions of ether followed. The ether extracts were dried over magnesium sulfate and distilled with an efficient column. There was obtained 19.5 g. (74%) of *β-n*-propylalloy alcohol, b.p. 62° (19 mm.), n^{20}D 1.4318.

Anal. Calcd. for $C_6H_{12}O$: C, 71.95; H, 12.08. Found: C, 71.70; H, 12.36.

***β-n*-Propylallyl Chloride.**—Essentially the procedure of Frazer, *et al.*,[5] was employed. To a solution of 5.9 g. of thionyl chloride in 50 ml. of dry ether at −10° was slowly added 19 g. (0.10 mole) of *β-n*-propylallyl alcohol and 7.6 g. of dry pyridine dissolved in 50 ml. of ether. Following the addition the mixture was warmed to room temperature and filtered to remove pyridinium chloride. The ether was removed from the filtrate and the residual oil added to 5.9 g. of thionyl chloride. The solution was heated to 70° for 2 hours, cooled, poured into 50 ml. of ice and water and the organic layer taken up in ether. The ether extract was washed well with water, dried over magnesium sulfate and distilled at atmospheric pressure with a small column. The product, b.p. 119–121°, n^{20}D 1.4357, weighed 12 g. (54%).

Anal. Calcd. for $C_6H_{11}Cl$: C, 60.76; H, 9.35. Found: C, 60.95; H, 9.50.

β-Benzylallyl Alcohol.—β-Benzylacrylic acid (23 g., 0.14 mole) prepared by the method of Mannich and Ganz[3] was reduced with 8 g. of lithium aluminum hydride as described above for the reduction of *β-n*-propylacrylic acid. The resulting product, 12.3 g. (58%), was obtained as an oil which boiled at 82° (0.50 mm.), n^{20}D 1.5359.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.90; H, 8.00.

β-Benzylallyl Chloride.—In 25 ml. of dry ether were placed 9.5 g. (0.065 mole) of pure β-benzyl allyl alcohol and 2.6 g. of dry pyridine. The resulting soultion was added at −10° and with stirring to a solution of 3.7 g. of thionyl chloride in 25 ml. of dry ether. The mixture was then warmed to room temperature, filtered and the ether solvent removed *in vacuo;* 3.7 g. of thionyl chloride was added to the residue and the resulting solution was heated to 70° for 2 hours. The crude product was poured into 50 ml. of ice and water and the organic layer taken up in ether, washed with water and dried over magnesium sulfate. Distillation with a small column afforded 8.2 g. (77%) of chloride which boiled at 68° (2 mm.), n^{20}D 1.5315.

Anal. Calcd. for $C_{10}H_{11}Cl$: C, 72.07; H, 6.65. Found: C, 72.03; H, 6.80.

β-Phenylallyl Alcohol.—A solution of 115 g. (0.66 mole) of β-phenylallyl acetate[2] in 250 ml. of dry ether was slowly added to a well stirred solution of 12 g. of lithium aluminum hydride in 800 ml. of dry ether at the reflux temperature. The reaction product was worked up in the usual fashion to afford 81 g. of β-phenylallyl alcohol (b.p. 105° (4 mm.), n^{20}D 1.5688). Hatch and Patton[2] report b.p. 116–118° (11 mm.) and n^{20}D 1.5675.

β-Phenylallyl Chloride.—Thirty grams of thionyl chloride was dissolved in 200 ml. of dry ether and cooled to −10°. A solution of 67 g. (0.50 mole) of β-phenylallyl alcohol and 38 g. of pyridine in 200 ml. of dry ether was added slowly with stirring. After the addition the mixture was filtered and the solvent removed *in vacuo*. The oily residue was then heated to 70° with an additional 30 g. of thionyl chloride for two hours. The crude product was cooled, treated with ice and water and isolated in the usual fashion. Distil-

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(6) H. C. Brown and B. C. SubbaRao, *J. Org. Chem.*, **22**, 1136 (1957).

lation with an efficient spinning-band column gave 45 g. (60%) of β-phenylallyl chloride boiling at 88–89° at 5 mm., n^{20}_{D} 1.5545. Hatch and Patton[2] report an identical boiling point and n^{20}_{D} 1.5550.

Cyclopropane and Methylcyclopropane Preparation.—Identical procedures were employed for the preparation of cyclopropane and methylcyclopropane. A 500-ml. three-neck flask was employed as the reaction flask.

One-half mole of allyl or β-methylallyl chloride was placed in 100 ml. of pure diglyme and the diborane generated from 10.1 g. of sodium borohydride and 52 g. of boron trifluoride etherate[6] was passed in with stirring at 0°. The system had been purged with dry nitrogen before the addition of diborane was commenced. Following the addition, the solution was allowed to stand at 0° for one hour and purged with dry nitrogen. A reflux condenser was attached to the outlet of the reaction flask which in turn was connected to a series of two Dry Ice-cooled traps. A pressure-equalized dropping funnel which contained a solution of 48 g. of sodium hydroxide in 200 ml. of water and carried a nitrogen inlet tube was attached to the reaction flask. The cooling bath was then removed from the reaction flask and the aqueous sodium hydroxide added slowly with vigorous stirring. The reaction mixture was allowed to warm to about 50°. The system was slowly swept with nitrogen after the addition of the base solution. The methylcyclopropane (20.0 g., 72%) or cyclopropane (9.0 g., 43%) was collected in one −80% trap and identified by infrared and mass spectra. Additional purification was made by passing the products through a 5% solution of potassium permanganate to remove traces of oxidizable impurities.

Procedure for the Preparation of Benzyl-, Phenyl- and *n*-Propylcyclopropane.—The procedure employed in the preparation of high boiling substituted cyclopropanes was essentially the same as that described above for the lower boiling members of the series. These reactions were carried out on an 0.10-mole scale. The diborane employed was generated from 2.0 g. of sodium borohydride and 10.5 g. of boron trifluoride etherate.[2]

One-tenth mole of the appropriate allyl chloride was dissolved in 30 ml. of dry ethyl ether, cooled to 0° and treated with diborane as described above. Following the addition, the reaction mixture was maintained at 0° and a solution of 10 g. of sodium hydroxide in 40 ml. of water was added. The two-phase system was stirred at room temperature for 30 minutes and the organic layer separated, washed with water, dried and distilled with a small spinning-band column. Table I reports yields and boiling points.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRITISH COLUMBIA]

Perfluoroalkyl Derivatives of Tin. I. Trimethyltrifluoromethyltin[1]

BY H. C. CLARK AND C. J. WILLIS

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The reaction of hexamethylditin with trifluoroiodomethane gives trimethyltrifluoromethyltin. Differences in behavior between this compound and similar known compounds of other elements are related to the more electropositive nature of tin. Thermal decomposition of trimethyltrifluoromethyltin appears to proceed *via* difluoromethylene radicals, since pyrolysis alone or with tetrafluoroethylene gives perfluorocyclopropane. Reaction of equimolar amounts of trimethyltrifluoromethyltin and chlorine removes one methyl group to give dimethyltrifluoromethyltin chloride.

Comparatively few compounds are known in which a perfluoroalkyl group is linked to a metallic atom. In particular, knowledge is lacking of derivatives of the metallic elements of groups IIIA and IVA, for which very extensive ranges of organometallic compounds are known. We now report the first synthesis of a trifluoromethyl derivative of tin, trimethyltrifluoromethyltin, which may be prepared by using the high reactivity of hexamethylditin, $(CH_3)_3Sn{\cdot}Sn(CH_3)_3$. This compound will react readily with oxygen, sulfur, halogens or alkyl halides, in each case with cleavage of the intermetallic bond. It has now been found that reaction with trifluoroiodomethane will occur according to the equation

$$(CH_3)_3Sn{\cdot}Sn(CH_3)_3 + CF_3I \longrightarrow (CH_3)_3SnI + (CH_3)_3Sn{\cdot}CF_3$$

The reaction was carried out under pressure in the absence of light at 80°, using excess trifluoroiodomethane as solvent, and was complete in 24 hours. Trimethyltrifluoromethyltin is a colorless liquid, b.p. 101°, having a faint smell similar to that of tetramethyltin. Its boiling point shows an increase of 24° over that of tetramethyltin, a much larger increase than the 5° rise which accompanies the exchange of one methyl group for trifluoromethyl in trimethyl-phosphine, -arsine or -stibine.[2] This large increase may be due to the more polar nature of the trifluoromethyl compound of tin, which is much more electropositive than the group V elements.

When the mechanism of the reaction of hexamethylditin with trifluoroiodomethane is considered it would be easy to suggest a radical mechanism with homolytic dissociation of the tin compound as the first step, *e.g.*

$$(CH_3)_3Sn{\cdot}Sn(CH_3)_3 \longrightarrow 2(CH_3)_3Sn{\cdot}$$

$$(CH_3)_3Sn{\cdot} + CF_3I \longrightarrow (CH_3)_3Sn{\cdot}CF_3 + I{\cdot}$$

$$(CH_3)_3Sn{\cdot}Sn(CH_3)_3 + I{\cdot} \longrightarrow (CH_3)_3SnI + (CH_3)_3Sn{\cdot}\ \text{etc.}$$

Such a process must be considered unlikely, however, in view of current opinion on the dissociation of hexamethylditin. Early workers,[3] on the basis of cryoscopic molecular weight measurements in dilute solution, regarded the molecule as largely dissociated into "trimethyltin." More recent magnetic measurements,[4] however, have shown that very little dissociation can be occurring, while as long ago as 1869 Ladenburg[5] found that the vapor density of hexaethylditin at 225° corresponded to the formula $(C_2H_5)_6Sn_2$. All workers agree that the complete absence of color in hexamethylditin or its solutions is strong evidence against its dissociation into radicals.

As an alternative reaction mechanism, an intermediate complex of hexamethylditin with trifluoroiodomethane may be postulated, which could

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(1) This work was supported by the U. S. Office of Naval Research.

(2) R. N. Haszeldine and B. O. West, *J. Chem. Soc.*, 3631 (1956).

(3) C. A. Kraus and W. V. Sessions, THIS JOURNAL, **47**, 2361 (1925).

(4) H. Morris and P. W. Selwood, *ibid.*, **63**, 2509 (1941).

(5) A. Ladenburg, *Ann. Suppl.*, **8**, 69 (1869).